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THE FRANKLIN INSTITUTE RESEARCH LABORATORIES
PHILADELPHIA, PA. 19103

CONTRACT DA-18-108AMC-169

FINAL REPORT

COVERING THE PERIOD

1 JUNE 1963 TO 27 JANUARY 1965

A NEW TYPE OF POLYMERIZATION INVOLVING ORGANOPHOSPHORUS COMPOUNDS AS CATALYSTS
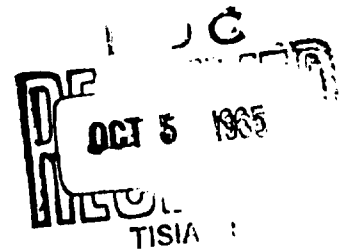
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ABSTRACT

The polymerization of N-vinylcarbazole is readily catalyzed by strong and weak Bronsted acids as well as diethylchlorophosphate and other compounds which hydrolyze to yield Bronsted acids. Polymerization occurs with catalyst concentrations as low as 40 parts per billion. There is a qualitative correlation between acidic and catalytic activities. The catalytic effect is greatest in non-protonic polar solvents such as acetonitrile and isobutyronitrile. Polymerization in these solvents is readily detected visually at an early stage by turbidity owing to insolubility of polymer formed. High conversion to polymer can be obtained within 30 secs. Water retards but oxygen and carbon dioxide, alone or together, do not influence the polymerization. Although not studied specifically, no effect of light on the Bronsted-acid catalyzed polymerization of N-vinylcarbazole was noted in the course of this work.

A kinetic study of the homogeneous polymerization with diethyl-chlorophosphate and diethylphosphoric acid in methylene chloride indicates that catalysis by diethylchlorophosphate involves both of the acids resulting from hydrolysis. The rate of hydrolysis is fast and does not control the rate of polymerization. With diethyl(p-nitrophenyl)phosphate as the catalyst, however, the polymerization is much slower. Here the slower hydrolysis of the catalyst controls the rate of polymerization. Formulation of a generally applicable rate expression is complicated by changes in the monomer dependency at high and low monomer concentrations. Increased dependence at high monomer concentration suggests that monomer aggregation may be a factor.

It is concluded that the polymerization of N-vinylcarbazole has unusual features which facilitate a unique susceptibility to catalysis by minute

traces of acids and acid-yielding compounds. The polymerization can be used to detect hydrolyzable phosphoric acid derivatives. Concomitant sensitivity to other acids in the atmosphere and those present as impurities in a solvent or other polymerization mixture components presents a disadvantage. However, it appears feasible to convey selective sensitivity to phosphoric acids by incorporating additives that deactivate other acids. For instance, addition of pinene can serve to prevent polymerization by hydrogen chloride without inhibiting polymerizations by diethylchlorophosphate and GB.

INTRODUCTION

The general objective of the overall program of which this contract is a part is to develop sensitive practical means of detecting toxic air contaminants. The specific objective of this contract is to determine the feasibility of detecting minute concentrations of contaminants by a chemical amplification method in which contaminants catalyze a readily detectable polymerization of a monomer such as N-vinylcarbazole. Polymerization of N-vinyl-carbazole with the simulating agent diethylchlorophosphate was found to involve catalysis by the acidic hydrolysis products of this compound.

There have been relatively few detailed investigations of Bronsted-acid-catalyzed polymerizations and none with N-vinylcarbazole as the monomer. "The Chemistry of Cationic Polymerization", edited by P. H. Plesch[1], is the most comprehensive critical review of this subject up to about 1962 that is available. A more recent and condensed review is given by Pepper[2] which lists and discusses many of the reactions involved in cationic polymerization and mechanisms proposed for them. Although qualitative observations have been recorded

for almost 200 years[2], there are few, if any, cationic polymerizations of which
the mechanism is well understood. This is, for instance, indicated by the fact
that even the most intensively studied cationic polymerizations such as those of
styrene[1] and isobutylene[1] continue to be favorite subjects of academic and
industrial studies. The mechanisms of various cationic polymerizations are
complex, involve a multitude of simultaneous and, often, instantaneous interactions,
vary from one another much more than in free radical polymerization, and depend
greatly on the types of monomer, catalyst, cocatalyst, solvent, impurities and
reaction conditions involved. Consequently, few guiding principles are generally
applicable. The present investigation, therefore, deals mostly with a study of
the characteristics of the Bronsted-acid-catalyzed polymerization of N-vinyl-
carbazole in order to develop the best conditions to induce polymerization with
extremely low concentrations of phosphorus-containing compounds without interference
from other possible air pollutants.

The polymerization of N-vinylcarbazole in acetonitrile is readily
detected at an early stage by the appearance of turbidity owing to the insolubility
of polymer in this solvent. This medium was used for qualitative and semi-
quantitative screening of the effects of various phosphorus compounds, acids,
air, oxygen and water on the polymerization (heterogeneous polymerization) in
preparation for a more detailed kinetic study using homogeneous reaction conditions
in methylene chloride and mixtures of this solvent with acetonitrile.

RESULTS AND DISCUSSION

I. GENERAL CONSIDERATIONS

Cationic polymerization can involve many interactions. A list
of reactions would have to include complex formations between catalyst, cocatalyst,
monomer and solvent, addition of protons, Lewis acids, carbonium- and other ions

to double bonds, primary, secondary and tertiary carbonium-ion formation from monomer and growing polymer chains, Wagner-Meerwein and other rearrangements of monomeric and polymeric carbonium ions, proton expulsions from unrearranged and isomerized carbonium ions, proton transfers from carbonium ions to the anion of the catalyst, to monomer (chain transfer), to solvent and to dead polymer, hydride-ion capture by carbonium-ions, reversible and irreversible associations and reactions of protons, Lewis acids and carbonium-ions with the anion of the catalyst and other gegenions, water, impurities and solvent, cyclization of growing carbonium ions (so-called conjunct polymerization), and crosslinking reactions. For vinyl monomers containing heteroatoms such a list would probably also have to include similar interactions involving hetero-onium ions. The importance of most of these and other interactions in the initiation, propagation and termination of cationic polymerization has recently been reviewed by Pepper[2].

Studies aimed at a detailed understanding of a cationic polymerization involve many difficulties. Plesch notes in this connection for instance, that there was a twenty year lapse between the first two important papers by Esso investigators on the polymerization of isobutene with aluminum chloride in spite of much work in the interval (ref. 1, p. 138). The overall result of a cationic polymerization that is usually observed is the net effect of many more or less interdependent interactions, having their own characteristics such as temperature and solvent dependencies, that occur more or less simultaneously and, often, instantaneously. A change in reaction conditions may, for instance, retard some of the intermediate interactions and promote others, complicating mechanistic interpretations of a change in the outcome of a polymerization. Minor modifications of reaction conditions can produce opposite net effects. For instance, with similar polymerizations of styrene, Hayes and Pepper[3] found catalyst to be

consumed and the rate of polymerization to be increasingly retarded as the polymerization progressed when sulfuric acid was used as the catalyst, whereas the catalyst was not consumed and the rate was not retarded when perchloric acid was used. Another example is the finding by Brown and Mathieson[4] that although a small amount of water promotes the polymerization of styrene with chloroacetic acids in several solvents, water retards the same polymerizations in nitromethane.

A common problem is that, ideally the purity of every reagent should be kept constant if they are used in experiments that are to be compared with one another, since the various interactions that occur in the course of a polymerization are likely to be affected by impurities in different ways. However, it is normally not known in advance how much reagent and time is needed to obtain the information being sought, and in most instances large batches of reagents cannot be kept stable or uncontaminated for very long. The purity problem also complicates evaluation of different findings by various investigators.

Since, furthermore, at the outset of this program, available information about the polymerization of N-vinylcarbazole with phosphorus compounds was limited mainly to observations that diethylchlorophosphate and a few other compounds catalyze the polymerization, the work had to be largely empirical and exploratory in nature. The experiments are reported in approximate order of performance. Most of the early experiments, with acetonitrile as the solvent in particular, served mainly to determine the qualitative effects of changing reaction conditions, and were conducted without a knowledge of the most suitable conditions needed for determining polymerization characteristics in a quantitative sense. For instance, in order to obtain information at the beginning of the program about the effects of catalyst and water concentrations, progressively varying amounts of these agents were added in several series of polymerizations. The trends shown by the results provide qualitative information about concentration

effects. The results are not considered to have significant quantitative value, particularly in cases involving addition of small amount of agents. These cases cannot be meaningful in a quantitative sense without a quantitative knowledge of concentrations of catalytic and retarding impurities contributed by all reaction components. This is illustrated by a sharp drop in conversion often observed as catalyst concentration was decreased. If, for instance, the catalyst is diluted ten times in each consecutive run of a series of polymerizations, it is reasonable to expect a sudden drop in conversion at a point at which the concentration of a retarding impurity becomes significant in relation to catalyst concentration. The level of impurities in reagents purified by standard procedures is usually too low for a quantitative determination. If, for instance, there was a chemical test as sensitive to traces of acids as the polymerization of N-vinylcarbazole, that test might have been studied for detection purposes instead of this polymerization.

Special purification procedures had to be developed. It was not until the conclusion of this program that a satisfactory method was developed for solvent purification. Consequently, most experiments involving the addition of a small amount of a reactant have mainly qualitative importance. Since our knowledge of favorable polymerization conditions remains incomplete, experimental results bearing on detection sensitivity and selectivity are probably too conservative in a quantitative sense.

II. HETEROGENEOUS POLYMERIZATION

A. Effects of Reagents and Reaction Conditions

Table I indicates the results of several qualitative test tube experiments in which a few drops or less of unpurified agents were added to solutions of N-vinylcarbazole in acetonitrile.

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TABLE I

QUALITATIVE EFFECTS OF VARIOUS AGENTS ON THE POLYMERIZATION OF N-VINYLCARBAZOLE IN ACETONITRILE

Compound[a]	Result
GA	no polymerization
GB (plant grade)	rapid polymerization
(purified by Melpar investigators)	slight turbidity
triethyl phosphate	no polymerization
triphenyl phosphate	slow but steady polymerization
dibutyl butylphosphonate	no polymerization
dipropylchloromethylphosphonate	no polymerization
diethyl phosphite	no polymerization
dibutyl phosphite	polymerization
benzene phosphorusoxychloride	rapid polymerization
diphenylphosphonylchloride	rapid polymerization
diethylchlorophosphate	rapid polymerization
dibutylchlorophosphate	rapid polymerization
diethyl phosphonic acid	rapid polymerization
dibutyl phosphoric acid	rapid polymerization
diethylpyrophosphoric acid	rapid polymerization
sulfuric acid	rapid polymerization
trichloroacetic acid	rapid polymerization
trifluoroacetic acid	rapid polymerization
conc. aqueous hydrogen bromide	some polymerization
hydrogen chloride	b
hydrogen fluoride	b
acetic acid	polymerization
phenol	polymerization
p-toluene sulfonylchloride	rapid polymerization
n-butylamine hydrochloride	no polymerization

[a] Compounds were used as received and purity was questionable except as indicated.

[b] Significant polymerization occurred only when monomer solutions were exposed to vapors of hydrogen halides. Very little polymerization occurred when hydrogen halides were dissolved in acetonitrile prior to addition of monomer.

This was one of the earliest experiments performed, at a time when nothing was known about reaction conditions required for meaningful experiments. The activity of GA was not, but should be redetermined. GB was an active catalyst in later experiments. The activity of triethylphosphate is probably due to hydrolysis products resulting from moisture contamination. Subsequent experiments confirmed the catalytic activity of weak acids such as phenol, acetic and benzoic acids.

One of the concerns in evaluating the potential capability of a polymerization system to detect traces of catalytic agents is whether catalyst is consumed in the course of polymerization, since consumption would cause the "chemical amplification" of the detection scheme to be limited largely by the molecular weight of the polymer produced. Chemical analysis of extracted polymers indicate that no catalytic residues are chemically incorporated in the polymer in the course of polymerization (Table II).

TABLE II

CATALYTIC RESIDUES CONTAINED IN SOXHLET EXTRACTED POLY-N-VINYLCARBAZOLE POLYMERS
PREPARED WITH DIETHYLCHLOROPHOSPHATE AND HYDROGEN CHLORIDE

Initiator[a]	Extraction Solvent	$\bar{M}_n$[b]	% Cl	% P	Cl atoms/ polymer chain	P atoms/ polymer chain	Cl atoms/ P atoms
diethylchloro-phosphate	methanol	4280	0.17	0.012	0.20	0.017	12
	cyclohexane	3150	0.03	0.00	0.03	0.00	0
hydrogen chloride	cyclohexane	4670	0.00		0.00		

[a] Unmeasured small amounts (amount of catalyst has no bearing on either elemental analyses of these polymers or correlation of analyses with molecular weight).

[b] Determined with a Mechrolab Vapor Osmometer.

The variations in retention of catalytic residues per polymer molecule indicate that their presence is due to physical retention and that exhaustive extraction

would remove all catalytic residues. This was not studied more extensively because the results were similar to those obtained with π-acid catalyzed polymerization of N-vinylcarbazole studied prior to this program. Lack of catalyst consumption is also indicated by the kinetics of the early stages of polymerization with Bronsted acids (discussed later in more detail), as well as by finding that on filtering off polymer obtained in a polymerization with diethylchlorophosphate,the filtrate could be used for a new polymerization. This procedure was repeated three times without noticeable loss in catalytic activity of the filtrate. Although chain initiation probably involves proton consumption, a lack in net consumption in the overall polymerization process is usually accounted for by proton elimination being a dominant termination reaction[1,2,3]. The absence of catalytic residues could then be accounted for by simultaneous departure of gegenion. Proton elimination is a common and, sometimes, a dominant termination and/or chain transfer reaction in cationic polymerization[1,2,3].

The rate of polymerization, however, is dependent on catalyst concentration as indicated by the results shown in Table III, and also on monomer concentration as indicated by the results shown in Table IV.

TABLE III

EFFECT OF DIETHYLCHLOROPHOSPHATE CONCENTRATION ON CONVERSION[a]

ml. diethylchlorophosphate	0.1	0.01	0.005	0.002	0.001	0.0001
% Conversion	54.0	30.4	30.9	0.7	0.5	0.2
	92.4[b]	12.5[b]	4.3[b]			

[a] Polymerization was performed with 0.20 g. N-vinylcarbazole in 5 ml acetonitrile and shortstopped after 30 secs., except as indicated.

[b] 0.71 g. N-vinylcarbazole in 5 ml. acetonitrile.

TABLE IV

EFFECT OF MONOMER CONCENTRATION ON CONVERSION[a]

gms. N-vinylcarbazole	0.200	0.160	0.120	0.080	0.040
% Conversion	47.6[b]	63.7	43.4	1.25	0.0[c]

[a] Polymerization was performed in 5 ml. acetonitrile with 0.1 ml. diethyl-chlorophosphate and shortstopped after 30 secs.

[b] Unknown amount of polymer lost in recovery.

[c] Appeared to contain some polymer; probably of low molecular weight.

The rate of polymerization is enhanced by allowing a solution of diethylchlorophosphate in acetonitrile to stand several days, whereas monomer aging has the opposite effect (Table V).

TABLE V

EFFECTS OF AGING SOLUTIONS OF DIETHYLCHLOROPHOSPHATE AND N-VINYLCARBAZOLE ON CONVERSION

ml acetonitrile	5	5	5	5	5	5
ml fresh diethyl-chlorophosphate	0.0001		0.100	0.100	0.010	0.010
ml aged diethylchloro-phosphate (1% solution in acetonitrile aged 2 days)		0.001				
gms. fresh monomer	0.20	0.20	0.20		0.20	
gms. aged monomer (4% solution in acetonitrile aged 3 days)				0.20		0.20
% conversion in 30 secs.	0.2	50.8	54	11	30.4	5.3

These results suggest absorption or generation of an impurity on standing. The catalytic activities of various fractions from a distillation of diethylchloro-phosphate suggest that the same impurity might be present in the material supplied by the vendor. The purest fraction is least active (Table VI).

TABLE VI

THE EFFECT OF FRACTIONATING DIETHYLCHLOROPHOSPHATE ON POLYMER CONVERSION[a]

Fraction:	fore cut	center cut[b]	end cut
% Conversion:	84.8	0.3	95.8
	73.1	0.0	96.2

[a] Duplicate 30 sec. runs with 0.1 ml catalyst and 0.2 g N-vinylcarbazole in 5 ml acetonitrile.

[b] 57°C/2.2 mm Hg

The activity of a distilled fraction is restored by exposure to the atmosphere (Table VII) or by addition of water (Table VIII).

TABLE VII

THE EFFECT OF CATALYST AGING ON POLYMER CONVERSION[a]

dist.$(C_2H_5O)_2P(O)Cl$:	old previously opened sample	unopened new sample	same new sample previously opened
% conversion	88.8	19.4	34.1

[a] 30 sec. polymerizations with 0.1 ml catalyst and 0.2 g N-vinylcarbazole in 5 ml acetonitrile

TABLE VIII

EFFECTS OF TREATING DIETHYLCHLOROPHOSPHATE WITH WATER AND OXYGEN ON POLYMER CONVERSION[a]

Treatment of catalyst:	none	oxygen[b]	water
% conversion	6.1	8.2	43.2
	15.8	6.2	45.1

[a] Duplicate 30 sec. polymerizations of 0.2 g N-vinylcarbazole in 4 ml acetonitrile to which 1 ml aliquots of variously treated 10% solutions of diethylchlorophosphate in acetonitrile were added.

[b] Oxygen was bubbled through 10% catalyst solution for 10 minutes.

[c] Solution of diethylchlorophosphate containing an equimolar amount of water.

It is also seen from the results shown in Table VIII that oxygen has no effect on the activity of the catalyst.

When water is added to a polymerization of N-vinylcarbazole with diethylchlorophosphate there is a sharp drop in conversion when the amount of water is in excess of that required for hydrolysis of the phosphorus compound (Table IX). This indicates that it is the acids resulting from hydrolysis of diethylchlorophosphate which are the actual catalysts for the polymerization and, furthermore, that water not consumed in the hydrolysis retards the polymerization.

TABLE IX

EFFECT OF ADDED WATER ON POLYMER CONVERSION[a]

ppm added water	0	500	1000	2000[b]	3000	4000
% Conversion	84.0	80.0	73.2	51.5	11.5	11.9

[a] Polymerization performed with 0.10 ml diethylchlorophosphate and 0.20 g N-vinylcarbazole in 5 ml acetonitrile and shortstopped after 30 secs.
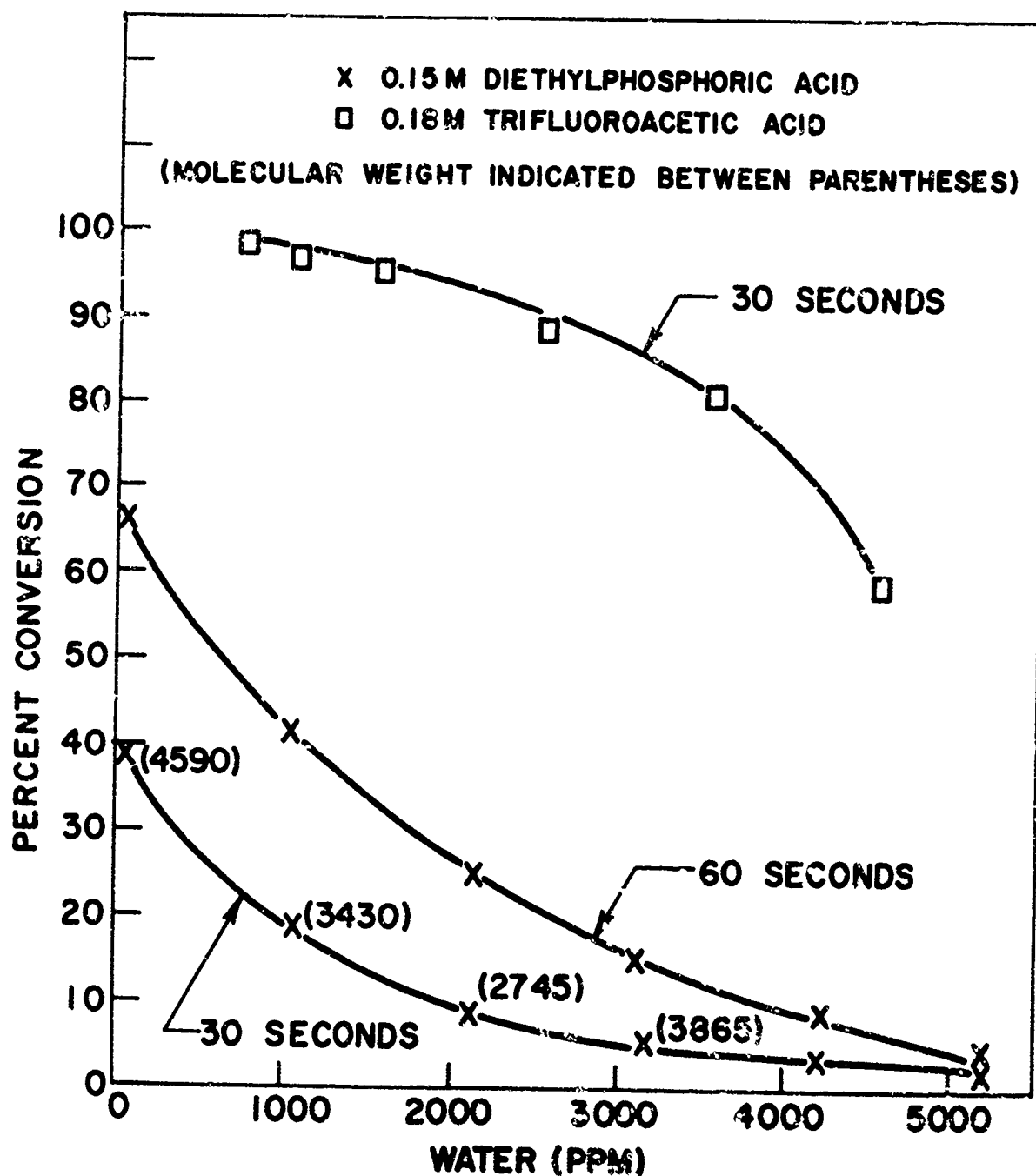
[b] Approximately equimolar to 0.10 ml diethylchlorophosphate.

The finding that slower hydrolyzing diethyl(p-nitrophenyl)phosphate (from American Cyanamid Co.) causes a very slow polymerization of N-vinylcarbazole in acetonitrile containing about 600 ppm water is a further indication that the catalysis by phosphoric acid derivatives involves the hydrolysis of these compounds before polymerization occurs. It took about 2 minutes after the addition of diethyl(p-nitrophenyl)phosphate for a slight turbidity to appear, about 9 minutes for the mixture to become opaque and about 20 minutes before a flashlight beam could not be seen through the mixture. The conversion was estimated to be about 5% or less at this stage. Since, as discussed later in more detail, the polymerization with one of the hydrolysis products in both cases, diethylphosphoric acid is only about 50% slower than the polymerization with an equimilar amount of diethyl-chlorophosphate, the much slower polymerization with diethyl(p-nitrophenyl)phosphate cannot be attributed to the other hydrolysis product formed being p-nitrophenol instead of hydrogen chloride from diethylchlorophosphate.

The effect of water retardation on conversion is offset by increasing time of polymerization with diethylphosphoric acid in acetonitrile (Fig. 1). At high water levels in particular, the rate of polymerization with diethylchlorophosphate in acetonitrile appears to be approximately inversely proportional to the water content, e.g. the conversions are about the same at 30 and 60 secs. with 2110 and 4200 ppm water respectively. It is also seen that changes in water content did not produce significant changes in molecular weight and, as discussed later, variations in water content were also not found to produce significant changes in molecular weight during polymerization in methylene chloride. These results indicate that water serves as a retarder which does not inhibit polymerization in solvents with different polarities and that water is not involved in reactions affecting propagation and termination. Different effects of water on polymerizations in acetonitrile catalyzed by diethylphosphoric acid and trifluoroacetic acid (Fig. 1) suggest that water affects initiation by associating with catalyst.

There is still some question about the catalytic activity in acetonitrile of hydrogen chloride, a hydrolysis product of diethylchlorophosphate. Only 0.6 - 5.1% conversion to polymer was obtained in 30 secs. when hydrogen chloride (0.11 M) was added to solutions of 0.2 g N-vinylcarbazole in 5 ml. acetonitrile containing 540 to 2540 ppm water, but hydrogen chloride is an effective catalyst when passed in the vapor state over a solution of monomer in acetonitrile and also, as discussed later in more detail, when formed in situ in a solution of monomer in methylene chloride. These observations suggest that there is a competing interaction of hydrogen chloride with acetonitrile which has a deactivating influence on the catalytic properties of hydrogen chloride. Drifting of the conductivity of solutions of hydrogen chloride in acetonitrile has also led other investigators to suspect that such an interaction

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FIG. I.

EFFECT OF WATER CONTENT ON CONVERSION WITH
0.21M N-VINYLCARBAZOLE IN ACETONITRILE

X 0.15 M DIETHYLPHOSPHORIC ACID
□ 0.18M TRIFLUOROACETIC ACID

(MOLECULAR WEIGHT INDICATED BETWEEN PARENTHESES)

occurs[5]. The polymerization results, however, indicate that the interaction
with acetonitrile does not compete effectively with the catalytic activity of
hydrogen chloride in polymerization when the times of exposure of hydrogen
chloride to monomer and solvent are the same.

The data shown in Fig. 1 also indicate that trifluoroacetic
acid is a more potent catalyst. A few qualitative tests indicated acetic acid
to be a less effective catalyst than trifluoroacetic acid or diethylphosphoric
acid. There appears to be a qualitative correlation between catalytic and
acidic activities in acetonitrile as indicated in Table X. However, acetonitrile
used in these experiments was found to contain an acidic impurity. Further
investigation indicated that this impurity can be removed by slowly passing
distilled acetonitrile through a column of powdered calcium hydride.

TABLE X

POTENTIOMETRIC READINGS (MILLIVOLT SCALE) PRODUCED BY INSERTION OF ELECTRODES OF
A pH METER INTO VARIOUS GRADES OF ACETONITRILE IN THE ABSENCE AND PRESENCE OF
VARIOUS SOLUTES

Solvent and Solutes	Initial	After 3-1/2 Hours
reagent grade acetonitrile	+ 268	+ 253
spectroquality acetonitrile	+ 17	+ 85
distilled spectroquality acetonitrile (P_2O_5)	− 175	− 48
0.076 M diethylphosphoric acid in distilled acetonitrile	− 337	− 341
0.075 M trifluoroacetic acid in distilled acetonitrile	− 445	− 481
0.175 M acetic acid in distilled acetonitrile	− 209	− 162
0.175 M acetic acid in spectroquality acetonitrile	− 118	− 102
0.559 M water in distilled acetonitrile	− 208	⊙ 131

Several tests with solid and gaseous carbon dioxide revealed
no catalytic properties. Carbon dioxide, therefore, could not have been the

contaminant which caused polymerization. The impurity may not have been removed when spectroquality acetonitrile was dried by distillation from phosphorus pentoxide prior to use. Although the acetonitrile used in this experiment came from Matheson Coleman and Bell and no specifications are available, impurity specifications for a similar grade of acetonitrile provided by Mallinkrodt Chemical Works indicate the presence of up to 300 ppm acetic acid. It is also possible that an acidic impurity was introduced by volatilization of phosphorus pentoxide in the distillation of acetonitrile (ref. 1, p. 683).

Although not studied specifically, no effects of light on the Bronsted-acid catalyzed polymerization of N-vinylcarbazole were noted. In another study, light was found to promote the polymerization of N-vinylcarbazole with π-acids or oxidants.

B. Detection Sensitivity

With 0.2 g. monomer (ca. 700 ppm H_2O) in 5 ml acetonitrile (ca. 600 ppm H_2O) precipitation of polymer could be observed to occur within 30 secs on addition of 20 ppm diethylchlorophosphate dissolved in acetonitrile.

In another test, the addition of 0.04 micrograms of diethyl-chlorophosphate in 0.1 ml methylene chloride (< 5 ppm H_2O) reproducibly formed within 13-14 mins. a visually detectable turbidity in a solution of 0.25 g. freeze dried N-vinylcarbazole (low H_2O content; could not be determined quantitatively) in 1 ml. acetonitrile (< 5 ppm H_2O). Similar control solutions in acetonitrile to which no catalyst was added did not become turbid until after about 60 mins. Solutions of the reagents spoiled soon after this test for reasons not fully understood, and no tests with lower catalyst levels were attempted.

When prepurified nitrogen was bubbled through vacuum distilled diethylchlorophosphate, flushed through the gas lines, and then passed over a 4% monomer solution in dried acetonitrile, a turbidity was produced within

30 secs. Without altering the gas stream, the reaction tube was then replaced

by a tube containing 2 ml of an aqueous sodium hydroxide solution to absorb

diethylchlorophosphate in the gas stream passed over it for 60 mins., after

which the solution was still basic. This solution contained 0.002% P and

0.045% Cl, indicating the introduction of 10^{-8} gram atoms P and 2×10^{-7} gram

atoms Cl during the 30 sec. polymerization interval. The excess of chlorine

over phosphorus content could be accounted for by preferential volatilization

of HCl produced by hydrolysis of diethylchlorophosphate as a result of the

presence of 10-20 ppm water in the nitrogen stream. As indicated below, further

inclusion of pinene in the monomer solution inhibits the hydrogen chloride –

but not the diethylchlorophosphate-catalyzed polymerization.

C. Selectivity

Several approaches to minimizing interference from the catalytic

effects of acids other than those resulting from in situ hydrolysis of diethyl-

chlorophosphate were considered. One approach involved using the thinnest sample

of Linde 5A molecular sieve impregnated paper[6] as a filter to remove moisture

and hydrogen chloride from a stream of nitrogen, which also contained diethyl-

chlorophosphate, before the stream came in contact with a solution of N-vinyl-

carbazole in isobutyronitrile. Preliminary tests indicated that the sieve-

impregnated paper was too dense to allow rapid diffusion of diethylchlorophosphate.

Another approach involved adding to the reaction mixture compounds

which might compete more effectively with N-vinylcarbazole in reactions with

acids such as hydrogen chloride than with diethylphosphoric acid produced by

in situ hydrolysis of diethylchlorophosphate. If, for instance, the additives

contain a double bond to which a proton can add, the resulting cation and,

consequently, the added proton, might not be stabilized until the cation derived

from the additive is neutralized by the further addition of an anion to form

a covalent adduct. It seems reasonable that a chloride anion might add more readily than a phosphate anion owing to steric and other factors.

Some qualitative tests indicated that carbodiimides might be useful additives. According to a literature survey[7], these compounds form adducts with inorganic and organic acids, water, alcohols, phenols, amines, thiols, acylhalides, isocyanates, epoxides, nitro and other active methylene group compounds, etc., on the basis of which it seemed that they might also serve to deactivate water and other impurities present in the system. A series of more quantitative tests, however, indicated that vacuum distilled samples of bis(2-methyl-phenyl)carbodiimide[7] and bis(2,6-diethylphenyl)carbodiimide[7], retarded polymerization by hydrogen chloride and diethylchlorophosphate and no useful distinctions could be discerned.

Experiments with pinene as an additive, however, appeared more promising as is indicated in Table XI. The distinction in the effects of

TABLE XI

EFFECT OF PINENE ON THE POLYMERIZATION OF N-VINYLCARBAZOLE CATALYZED BY DIETHYL-CHLOROPHOSPHATE AND HYDROGEN CHLORIDE

Agent[1]	Monomer	Solvent[2]	Pinene[3]	Time (secs)[4]
$(C_2H_5O)_2P(O)Cl$	0.12	2.0	—	5.4 ± 0.0
HCl	0.12	2.0	—	7.0 ± 0.5
$(C_2H_5O)_2P(O)Cl$	0.12	1.6	0.4	49.2 ± 2.5
HCl	0.12	1.6	0.4	> 300[5]

(1) The agent was introduced by bubbling nitrogen through either pure diethylchlorophosphate or concentrated HCl solution.

(2) Isobutyronitrile, distilled from di-o-tolylcarbodiimide.

(3) As received from Matheson, Coleman and Bell Co.

(4) Time to produce turbidity in solution due to polymer formation. Average of three runs.

(5) Dark color developed after 210 secs. One of the monomer solutions was exposed to HCl for 1/2 hr. and no polymerization occurred.

diethylchlorophosphate and hydrogen chloride was reproduced in further experiments with newly prepared reagents. A test at the Army Chemical Center, Edgewood, Md., indicated that addition of pinene can serve to provide a similar distinction between the effects of GB and hydrogen chloride.

D. Stability of Monomer Solutions

This study is handicapped by solutions of monomer being affected on standing by very minute traces of impurities that catalyze, retard or inhibit polymerization to an atypical degree. Even spectroquality and other high grade solvents that are commercially available appear to contain sufficient water and acidic impurities to affect polymerization. Depending on the method used for purification, solutions of monomer in nitriles have become turbid due to polymer formation on standing for a day, or longer in the presence of water, or became inactive with respect to acid catalysis on standing a week or more. The turbidity was obtained with solvents that were distilled from phosphorus pentoxide and passed through a column of finely powdered calcium hydride. This was very time consuming, and the procedure was changed to distillation from calcium hydride which led to monomer solutions that became inactive on standing. As a result, no worthwhile stability information was obtained. To check possible conversion of monomer to non-polymeric products, since Ellinger[8] has reported conversion to 1,2-trans-dicarbazylcyclobutane in methanol in the presence of p-chloranil and light, one of the solutions of N-vinylcarbazole in calcium-hydride-treated isobutyronitrile was worked up. Monomer was recovered in almost quantitative yield. It is suspected that traces of acids remain after phosphorus pentoxide-calcium hydride treatment, and, possibly, traces of amine after the treatment involving only calcium hydride. There is little doubt that the instability of

monomer dissolved in these solvents was due to impurities, since at the
conclusion of this program monomer solutions that remained stable and active
for at least five days were made with acetonitrile and isobutyronitrile that
had been refluxed with and distilled from bis(2-methylphenyl)carbodiimide[7].
This procedure is now being used successfully in another study of a cationic
polymerization of N-vinylcarbazole with other types of catalysts. A further
protection against the effects of acidic solvent impurities in a detection
device can be provided by including an additive such as pinene, which was found
to deactivate hydrogen chloride.

E. Miscellaneous Solvents

Solvents other than acetonitrile, isobutyronitrile and methylene
chloride were not studied extensively, and preliminary findings were unsatisfactory.

No polymerization with diethylchlorophosphate as the catalyst
occurred in reagent grade dimethylsulfoxide, and in a similar grade of glutaronitrile
the precipitation of polymer was slow. An attempt to use a 25 wt. % solution of
N-vinylcarbazole in a film of polyacrylonitrile cast on a glass plate from a
solution in dimethylformamide was unsuccessful. The film was vacuum dried at
room temperature (to prevent premature polymerization of monomer) for several
days. It had a milky appearance and adhered strongly to the glass plate. Contact
with diethylchlorophosphate in the vapor or liquid state had no visible effect
on the appearance of the film.

III. HOMOGENEOUS POLYMERIZATION

It was realized that acetonitrile might not be a suitable
solvent for detailed kinetic studies owing to possible complications arising
from the fact rate of polymerization and precipitation of polymer during
polymerization. This led us to study the homogeneous polymerization in methylene
chloride in which polymer remains dissolved as it is formed. It can be seen from
Fig. 2 that the polymerization in methylene chloride is slower than that in

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FIG. 2.
POLYMERIZATION OF 0.21M N-VINYLCARBAZOLE
WITH 0.15M DIETHYLPHOSPHORIC ACID IN
ACETONITRILE AND METHYLENE CHLORIDE
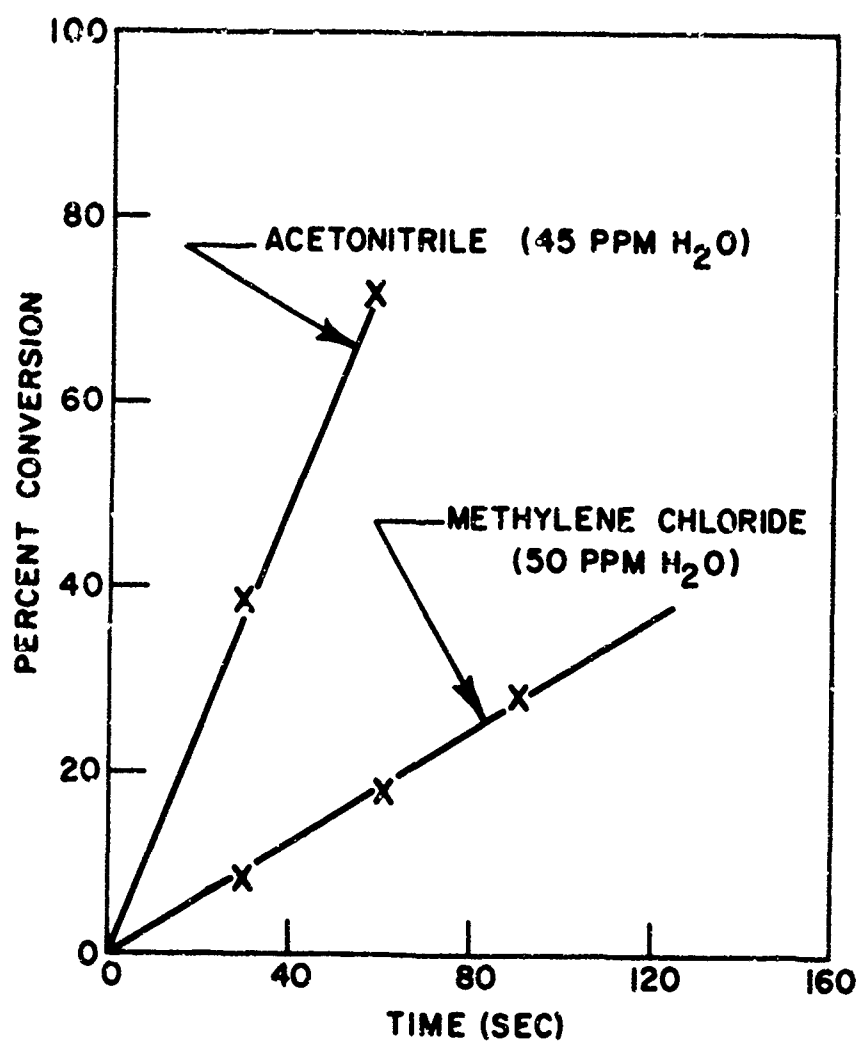
acetonitrile. This is consistent with previous findings that ionic polymerizations are slowest in solvents with the poorest ion-solvating properties[1,2]. This effect is generally attributed to a greater degree of pairing of oppositely charged ions in solvents with poor ion-solvating properties, hindering access of monomer to cations in cationic polymerization[1,2] or, conversely, to anions in anionic polymerization[9]. The overall effect of solvent on cationic polymerization is the net result of solvent effects on many interactions such as those indicated in the first discussion section of this report. In view of the complexities involved, a detailed study of these effects is considered to be beyond the scope of the present investigation.

It is known in some cases that the polarity or ion-solvating properties of a solvent can have a profound effect on an ionic polarization. For instance, the catalysis of the anionic polymerization of isoprene with lithium metal on lithium alkyls is much less stereospecific in ethers than in hydrocarbons[9], and, in the cationic polymerizations of styrene with chloroacetic acids, small amounts of water have been found to accelerate polymerization in several solvents but to retard polymerization in nitromethane[4]. Our findings, however, indicate that acid-catalyzed polymerizations of N-vinylcarbazole in acetonitrile and methylene chloride are qualitatively similar with respect to effects of monomer, catalyst and water. The results shown in Table XII indicate that water retards the polymerization in methylene chloride.

Time-conversion plots for five polymerizations in methylene chloride and three polymerizations in a 6/1 mixture of methylene chloride and acetonitrile are shown in Figs. 3 and 4 respectively. The observed initial rates of polymerization for these and other runs are shown in Table XIII. Calculated overall rate constants are not shown because no generally applicable rate expressions were found. However, some polymerization characteristics are

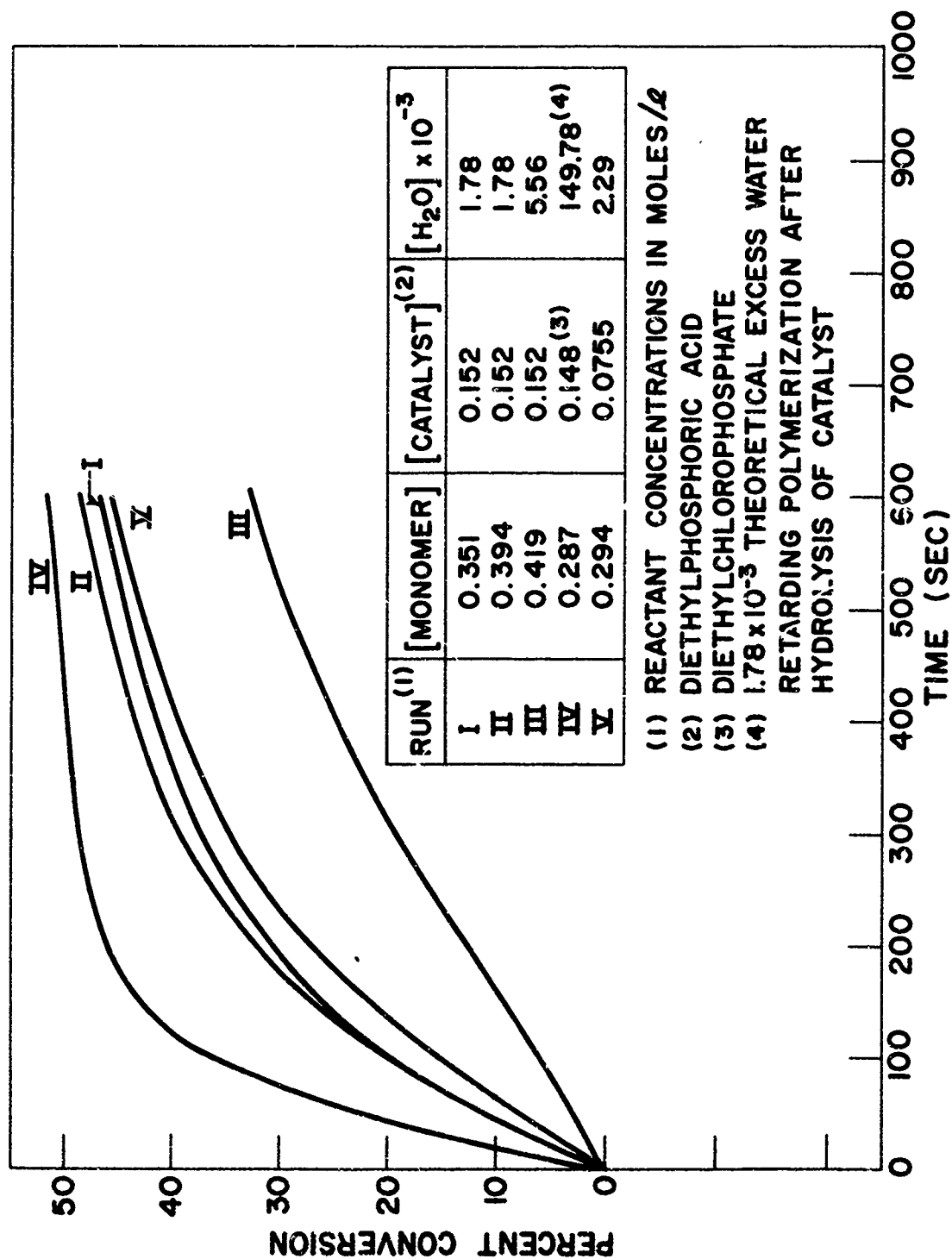FIG. 3. POLYMERIZATIONS OF N-VINYLCARBAZOLE IN
METHYLENE CHLORIDE AT 25°C

RUN[1]	[MONOMER]	[CATALYST][2]	$[H_2O] \times 10^{-3}$
I	0.351	0.152	1.78
II	0.394	0.152	1.78
III	0.419	0.152	5.56
IV	0.287	0.148[3]	149.78[4]
V	0.294	0.0755	2.29

(1) REACTANT CONCENTRATIONS IN MOLES/ℓ
(2) DIETHYLPHOSPHORIC ACID
(3) DIETHYLCHLOROPHOSPHATE
(4) 1.78×10^{-3} THEORETICAL EXCESS WATER
RETARDING POLYMERIZATION AFTER
HYDROLYSIS OF CATALYST

FIG. 4. POLYMERIZATIONS OF N-VINYLCARBAZOLE IN METHYLENE CHLORIDE/ACETONITRILE (6/1) AT 25°C

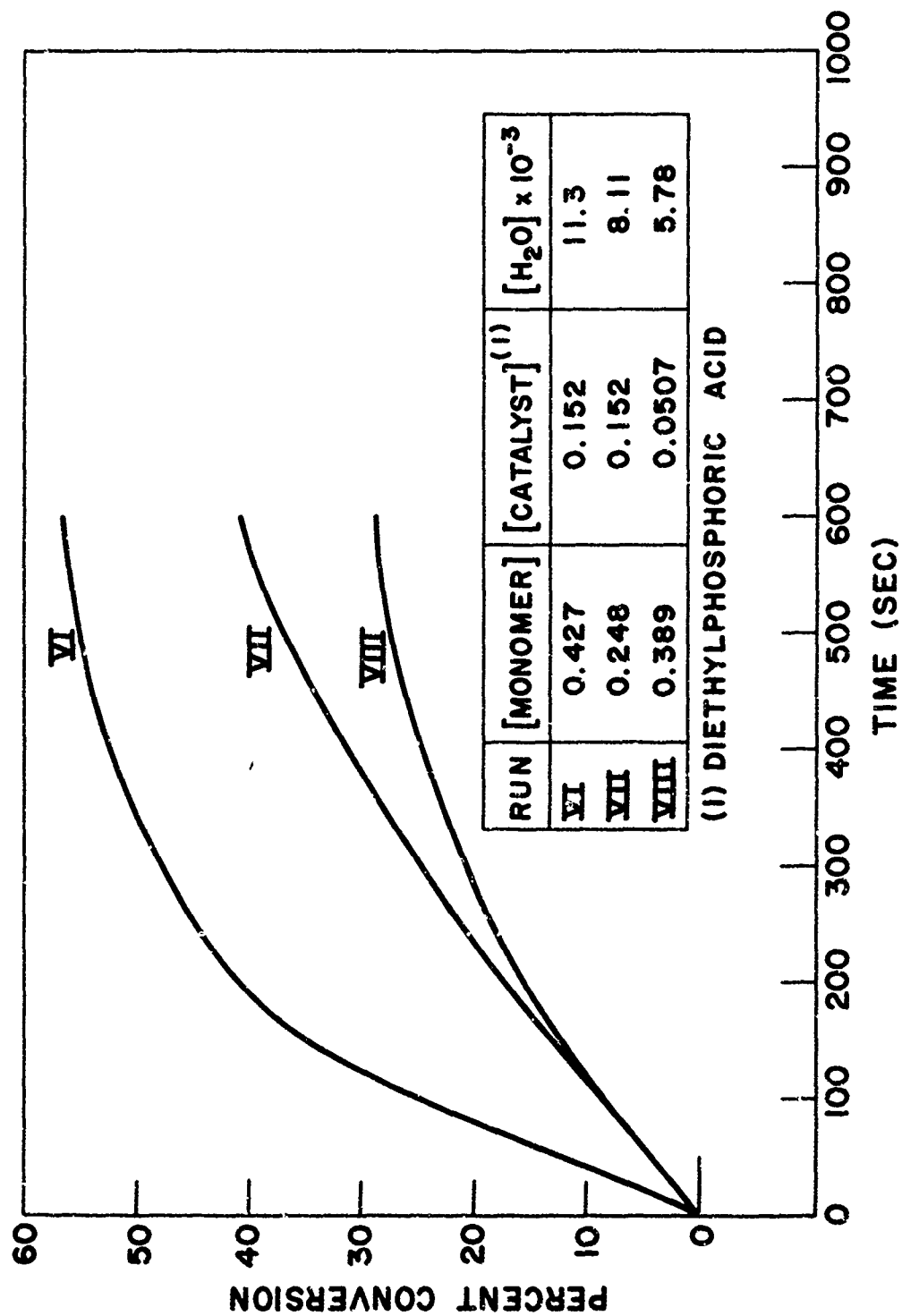| RUN	[MONOMER]	[CATALYST][1]	[H_2O] x 10^{-3}
VI	0.427	0.152	11.3
VII	0.248	0.152	8.11
VIII	0.389	0.0507	5.78

(1) DIETHYLPHOSPHORIC ACID

TABLE XII

EFFECTS OF TIME AND WATER CONTENT ON POLYMER CONVERSION IN POLYMERIZATIONS WITH
DIETHYLPHOSPHORIC ACID IN METHYLENE CHLORIDE[a]

gms. monomer	0.209	0.187	0.219	0.190	0.203	0.212
ppm water[b]	51	47	53	475	478	480
time (secs)	30	60	90	30	90	360
% conversion	7.9	18.6	23.6	1.7	4.8	24.5

[a] Polymerizations performed in 5 ml of a 0.15 M solution of diethylphosphoric acid in methylene chloride.

[b] Total water content including that which is introduced by the monomer, the original content of the solvent and added water.

apparent. A comparison of the data for runs II and III indicates that the rate of polymerization is inversely proportional to water concentration. The faster rate of homogeneous polymerization of run VIII than that of run III in spite of a significantly lower catalyst concentration indicates that increasing the polarity of the solvent medium favors a faster rate of polymerization. This effect contributes to the faster rate of the previously discussed heterogeneous polymerization in acetonitrile. Precipitation of polymer may be another factor contributing to faster polymerization in this latter solvent.

For conversions up to about 20%, straight line plots are obtained when t is plotted against $1/M^{a-1}$ where M is the monomer concentration at time t, and a increases from 3/4 to 5 with increasing monomer concentration (Figs. 5A – 5L) indicating lack of water and catalyst consumptions at this stage of the polymerization. The absence of phosphorus and chlorine in the polymer (Table II) and continued catalytic activity of solutions from which polymerized monomer was filtered off, also indicate that no catalyst is consumed during the polymerization. However, the water content after polymerization has been noted

TABLE XIII

OBSERVED INITIAL RATES OF POLYMERIZATION WITH DIETHYLPHOSPHORIC ACID AS THE CATALYST

Run	Solvent	[Mon.](m/l)	[Acid](m/l)	$[H_2O] \times 10^3$ (m/l)	$Ri \times 10^4$ (m/l sec)
I	Methylene Chloride	0.351	0.152	1.78	7.87
II	" "	0.394	0.152	1.78	8.45
III	" "	0.419	0.152	5.56	2.68
IX	" "	0.595	0.152	3.41	13.50
X	" "	0.610	0.152	3.31	14.37
XI	" "	1.14	0.152	10.9	37.1
XII	" "	0.139	0.152	—	2.19
IV[1]	" "	0.287	0.296[1]	1.78[2]	14.59
V	" "	0.294	0.0755	2.29	4.62
VI	Methylene Chloride-Acetonitrile[3]	0.427	0.152	11.3	10.49
VII	"	0.248	0.152	8.11	1.92
VIII	"	0.389	0.0507	5.78	3.33

(1) Diethylchlorophosphate (ECP) was used as the catalyst; [ECP] = 1/2 [Acid] = 0.148 m/l.
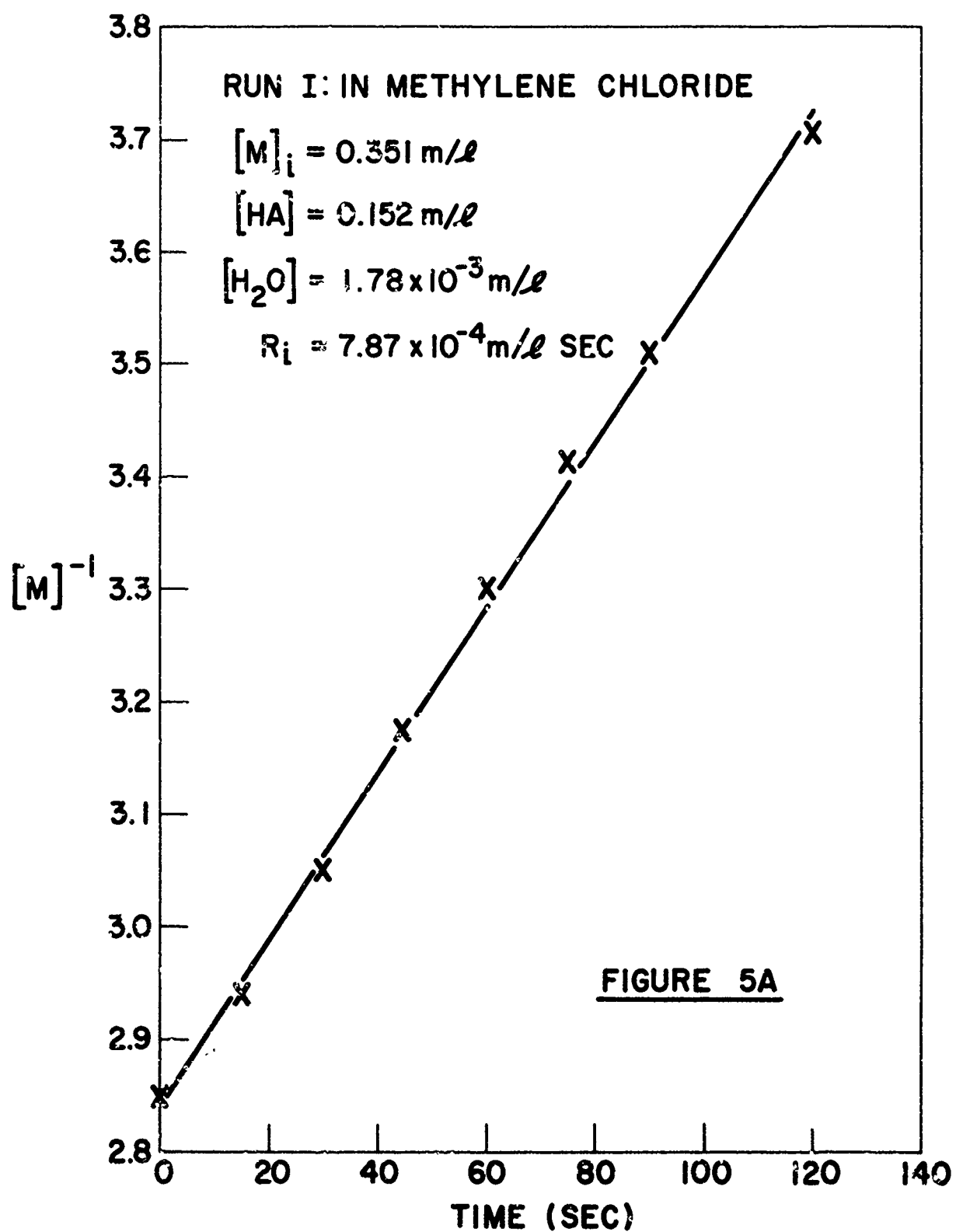
(2) Theoretical amount of water retarding polymerization after 0.148 m/l of 0.14978 m/l water actually added was consumed by hydrolysis of 0.148 m/l ECP.
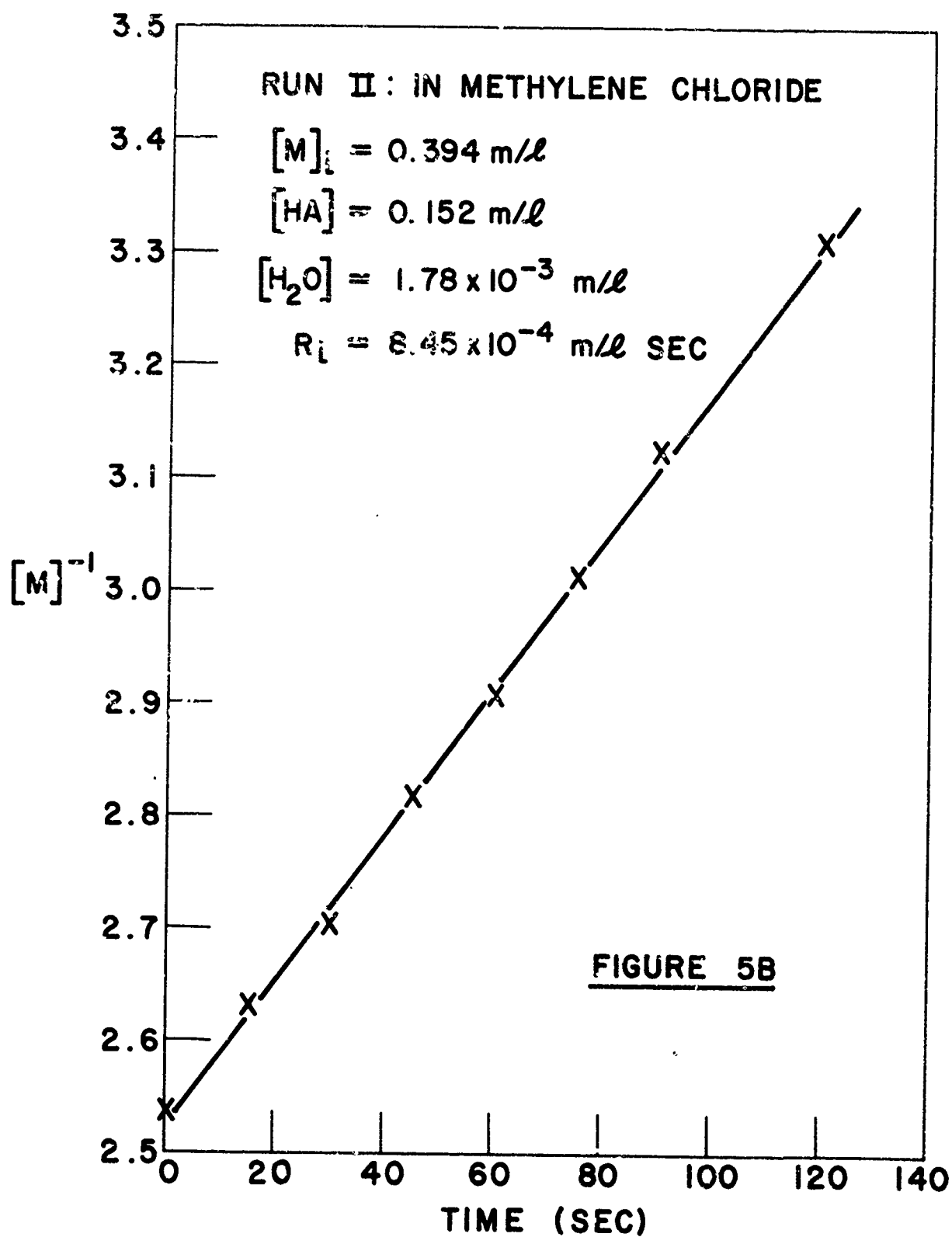
(3) Methylene chloride/acetonitrile = 6/1 by volume. Polymer precipitates at smaller ratios.
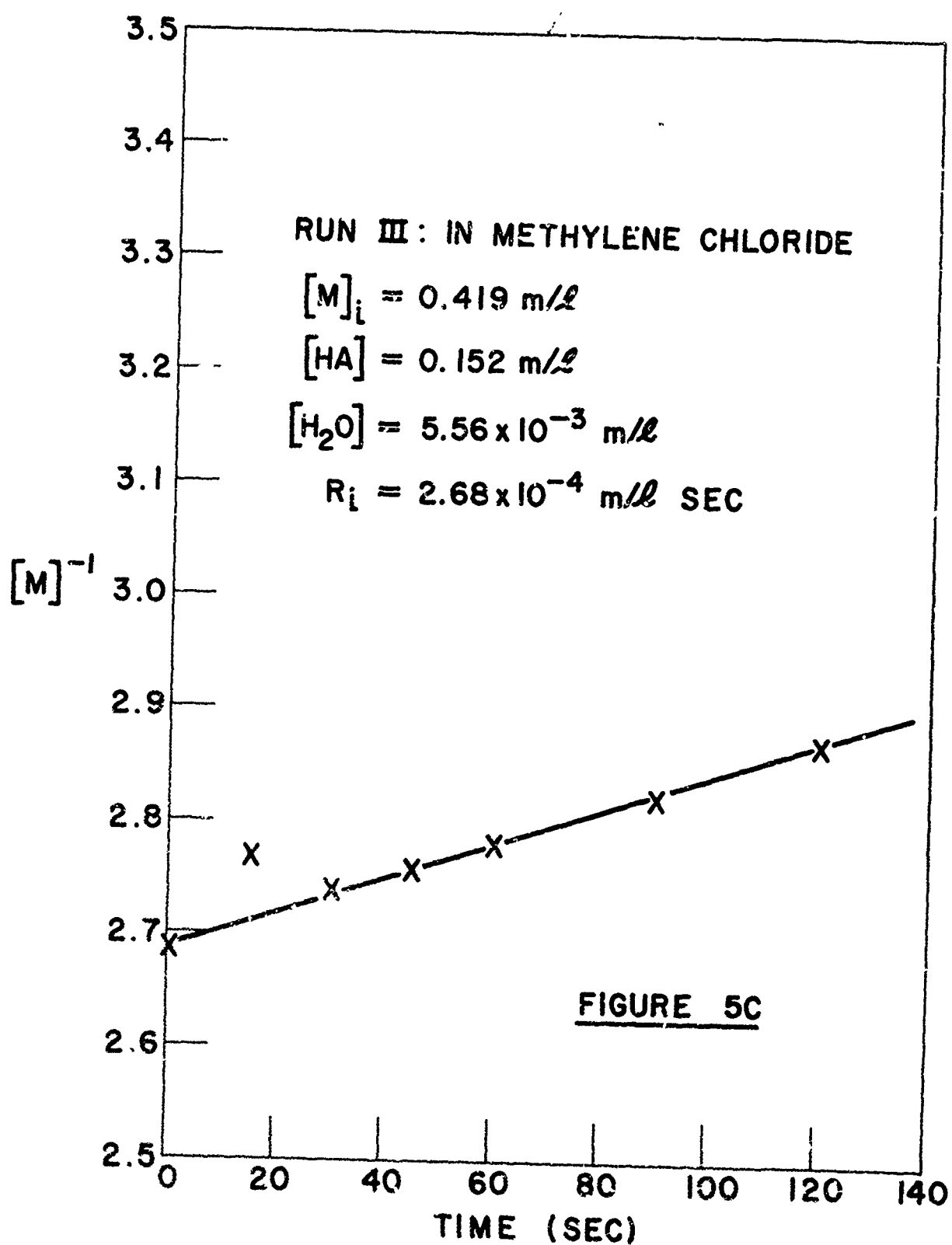
to be much lower (< 5 ppm) than it was initially (even when initial content was 150-200 ppm). It is not clear whether this water consumption occurs during or after polymerization, but the data in Table XIV indicate that no water consumption occurs during the initial phase of the polymerization with which we are primarily concerned.
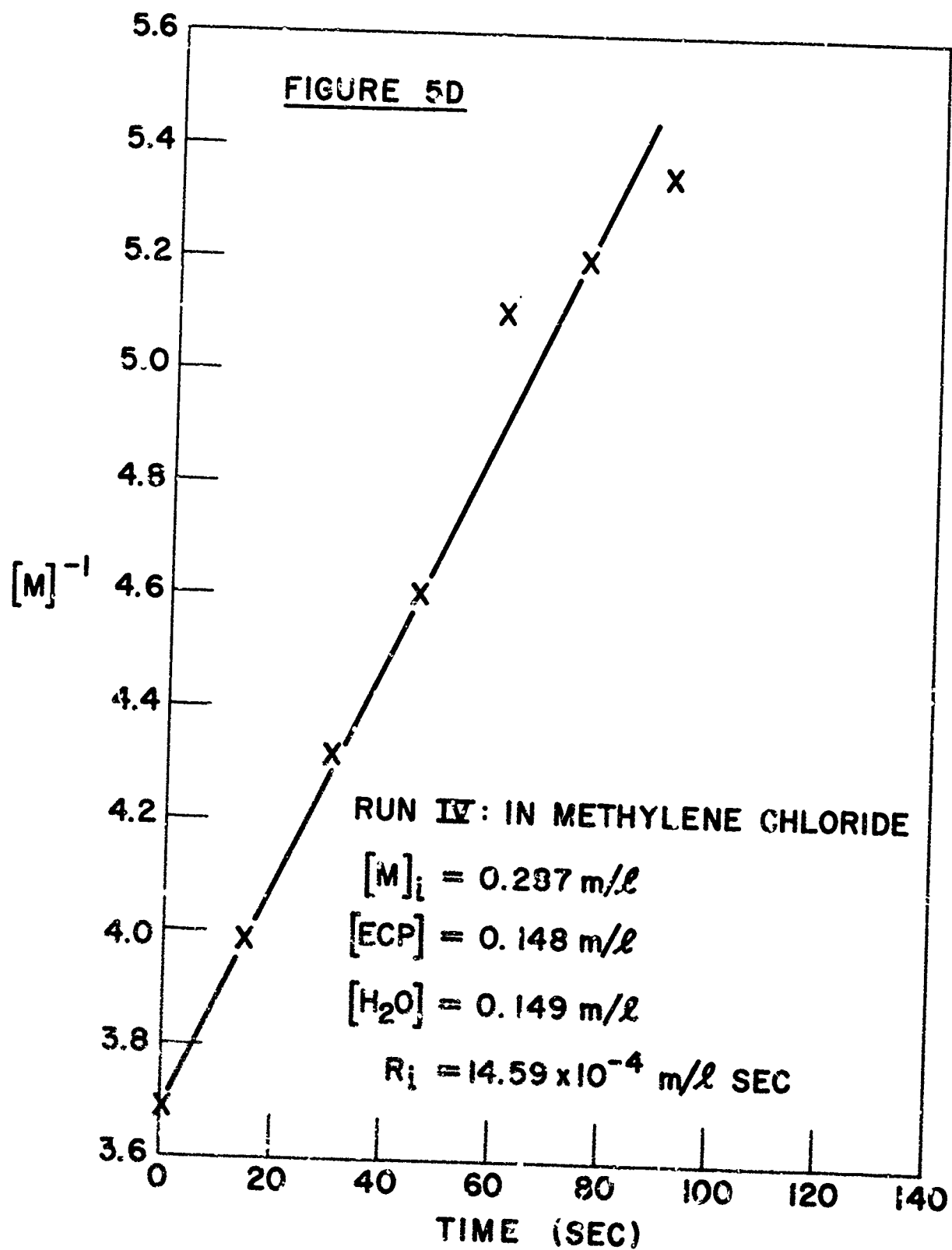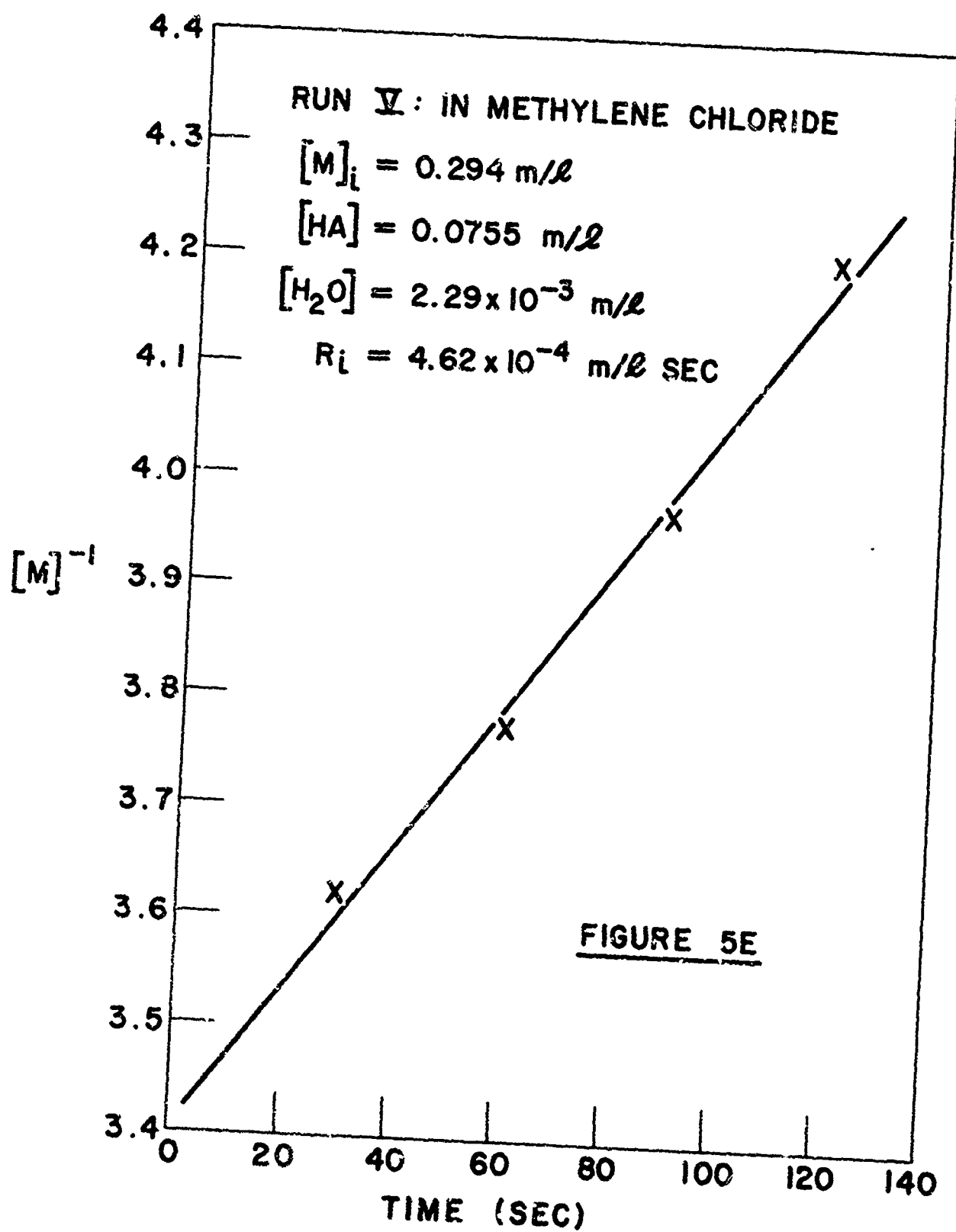
FIGS. 5A TO 5L

MONOMER DEPENDENCIES OF POLYMERIZATIONS
WITH VARIOUS INITIAL MONOMER CONCENTRATIONS
IN METHYLENE CHLORIDE AND 5/1 MIXTURE OF
METHYLENE CHLORIDE AND ACETONITRILE,
CATALYZED BY DIETHYLPHOSPHORIC ACID (HA)
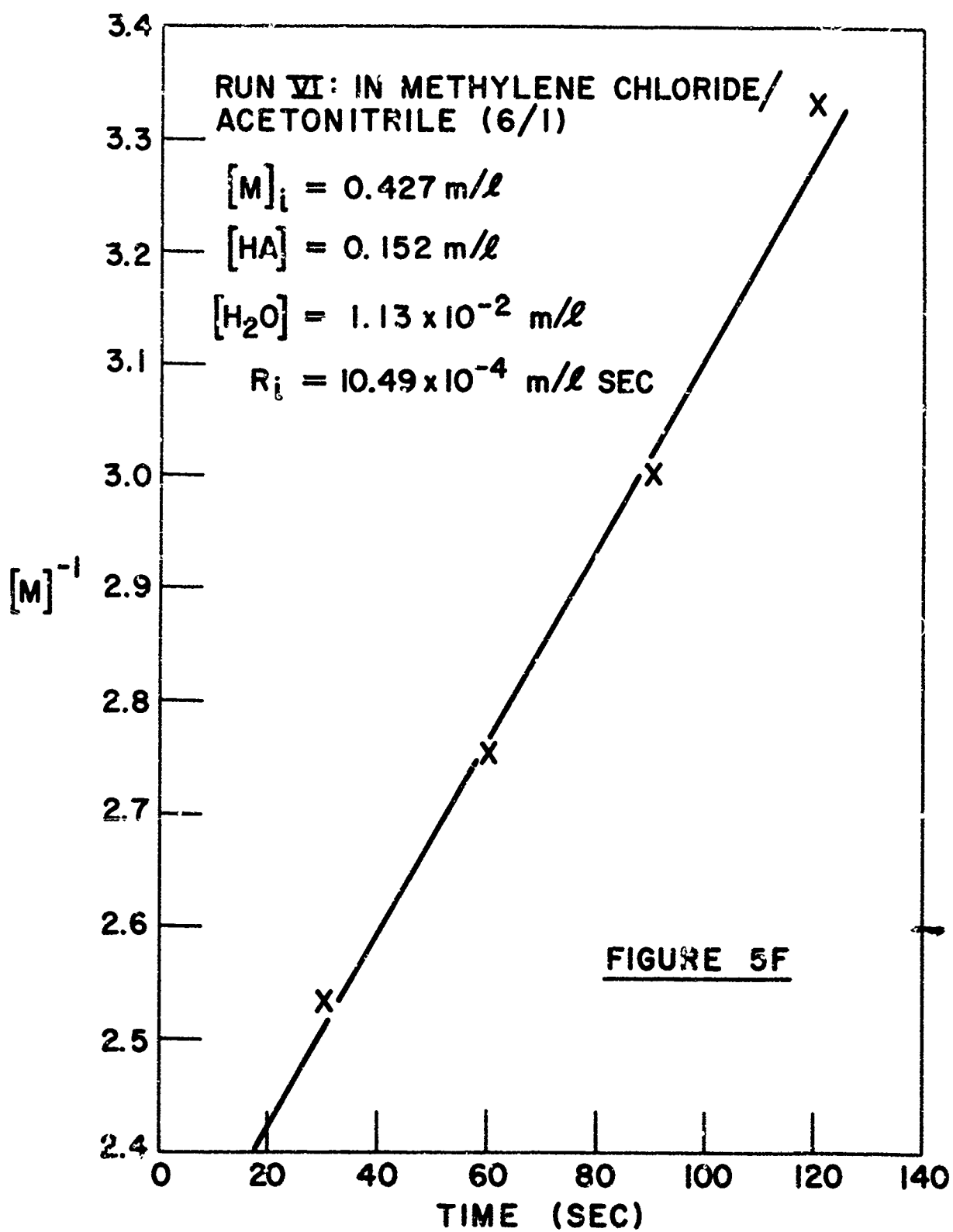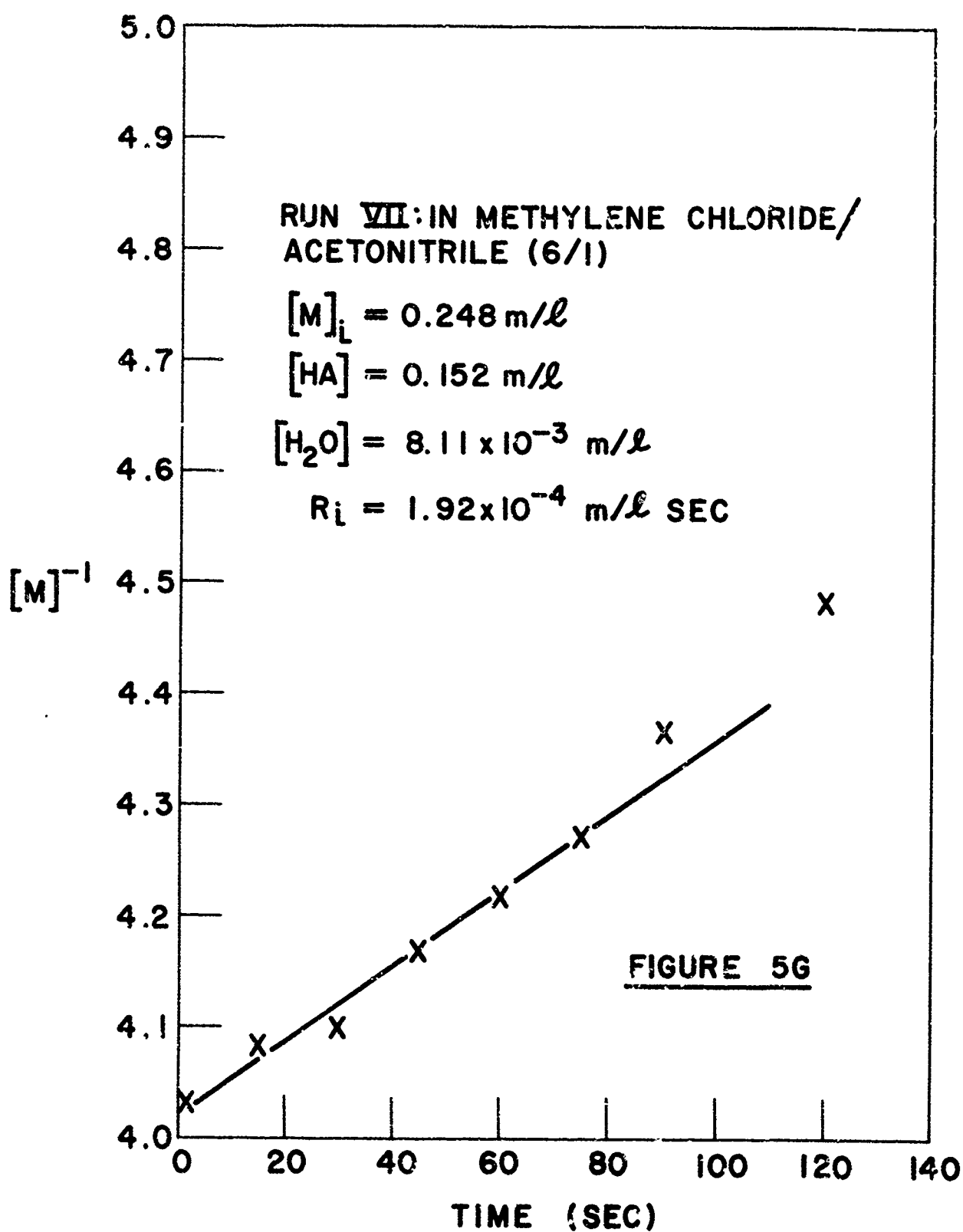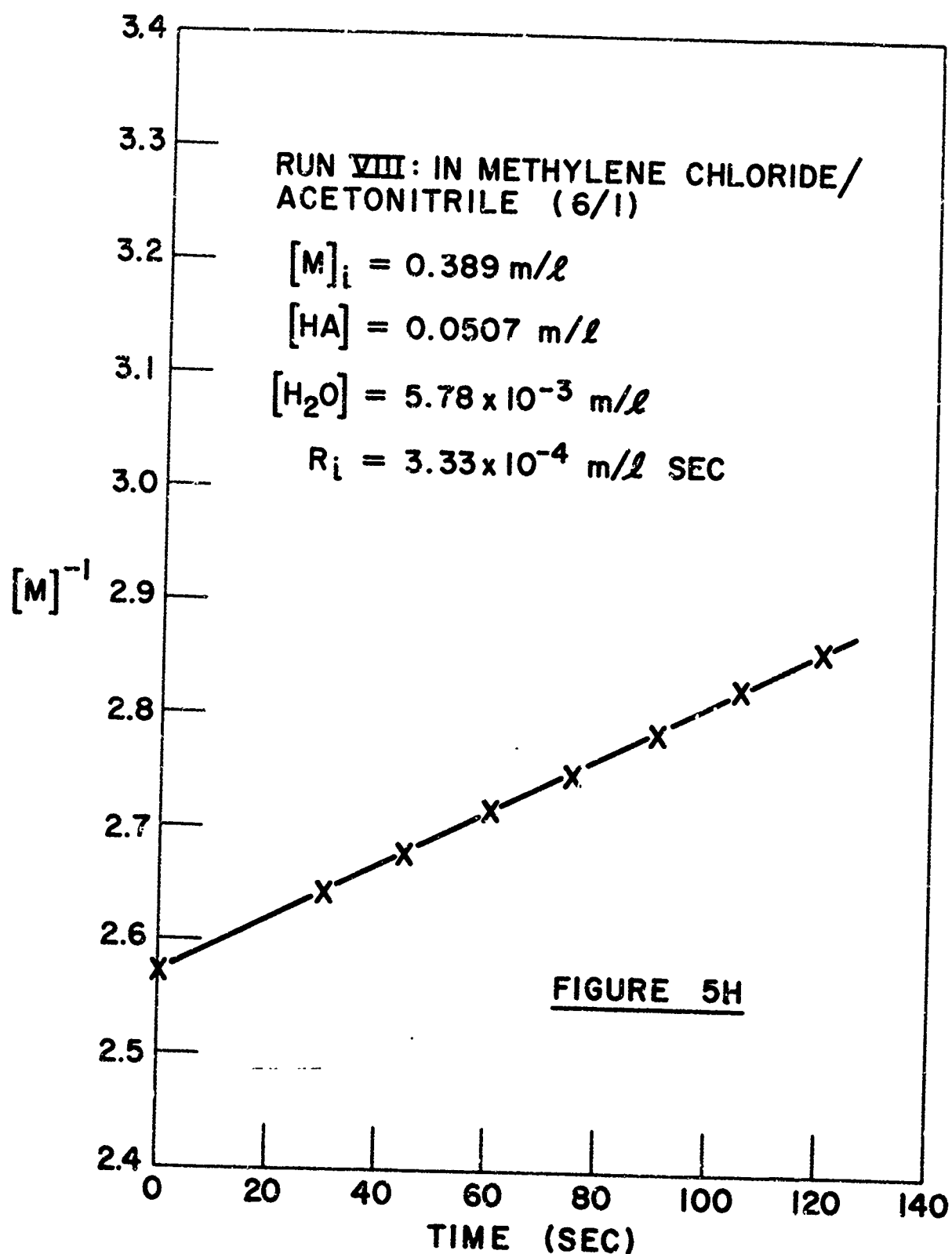AND DIETHYLCHLOROPHOSPHATE (ECP)

RUN I: IN METHYLENE CHLORIDE

$[M]_i = 0.351 \, m/\ell$

$[HA] = 0.152 \, m/\ell$

$[H_2O] = 1.78 \times 10^{-3} \, m/\ell$

$R_i \approx 7.87 \times 10^{-4} \, m/\ell \, SEC$

FIGURE 5A

$[M]^{-1}$

TIME (SEC)

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RUN II: IN METHYLENE CHLORIDE

$[M]_i = 0.394$ m/l

$[HA] = 0.152$ m/l

$[H_2O] = 1.78 \times 10^{-3}$ m/l

$R_i = 8.45 \times 10^{-4}$ m/l SEC

$[M]^{-1}$

TIME (SEC)

FIGURE 5B

RUN Ⅲ: IN METHYLENE CHLORIDE

$[M]_i = 0.419$ m/ℓ

$[HA] = 0.152$ m/ℓ

$[H_2O] = 5.56 \times 10^{-3}$ m/ℓ

$R_i = 2.68 \times 10^{-4}$ m/ℓ SEC

FIGURE 5C

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FIGURE 5D

RUN IV: IN METHYLENE CHLORIDE

$[M]_i = 0.237$ m/ℓ

$[ECP] = 0.148$ m/ℓ

$[H_2O] = 0.149$ m/ℓ

$R_i = 14.59 \times 10^{-4}$ m/ℓ SEC

Y-axis: $[M]^{-1}$

X-axis: TIME (SEC)

RUN V: IN METHYLENE CHLORIDE

$[M]_i = 0.294$ m/ℓ

$[HA] = 0.0755$ m/ℓ

$[H_2O] = 2.29 \times 10^{-3}$ m/ℓ

$R_i = 4.62 \times 10^{-4}$ m/ℓ SEC

$[M]^{-1}$

TIME (SEC)

FIGURE 5E

RUN VI: IN METHYLENE CHLORIDE/ ACETONITRILE (6/1)

$[M]_i = 0.427 \ m/\ell$

$[HA] = 0.152 \ m/\ell$

$[H_2O] = 1.13 \times 10^{-2} \ m/\ell$

$R_i = 10.49 \times 10^{-4} \ m/\ell \ SEC$

FIGURE 5F

$[M]^{-1}$

TIME (SEC)

RUN VII: IN METHYLENE CHLORIDE/
ACETONITRILE (6/1)

$[M]_i = 0.248 \ m/\ell$

$[HA] = 0.152 \ m/\ell$

$[H_2O] = 8.11 \times 10^{-3} \ m/\ell$

$R_i = 1.92 \times 10^{-4} \ m/\ell \ SEC$

FIGURE 5G

$[M]^{-1}$

TIME (SEC)

RUN VIII: IN METHYLENE CHLORIDE/
ACETONITRILE (6/1)

$[M]_i = 0.389 \text{ m/}\ell$

$[HA] = 0.0507 \text{ m/}\ell$

$[H_2O] = 5.78 \times 10^{-3} \text{ m/}\ell$

$R_i = 3.33 \times 10^{-4} \text{ m/}\ell \text{ SEC}$

FIGURE 5H

RUN IX: IN METHYLENE CHLORIDE

$[M]_i = 0.595$ m/ℓ

$[HA] = 0.152$ m/ℓ

$[H_2O] = 3.41 \times 10^{-3}$ m/ℓ

$R_i = 13.5 \times 10^{-4}$ m/ℓ SEC

FIGURE 51

$[M]^{-1}$

TIME (SEC)

RUN X : IN METHYLENE CHLORIDE

$[M]_i = 0.610$ m/ℓ

$[HA] = 0.152$ m/ℓ

$[H_2O] = 3.31 \times 10^{-3}$ m/ℓ

$R_i = 14.37 \times 10^{-4}$ m/ℓ SEC

FIGURE 5J

$[M]^{-1}$ (y-axis)

TIME (SEC) (x-axis)

RUN XI : IN METHYLENE CHLORIDE

$[M]_i = 1.140 \ m/\ell$

$[HA] = 0.152 \ m/\ell$

$[H_2O] = 1.03 \times 10^{-2} \ m/\ell$

$R_i = 37.1 \times 10^{-4} \ m/\ell \ SEC$

FIGURE 5K

$[M]^{-4}$

TIME (SEC)

RUN XII: IN METHYLENE CHLORIDE

$[M]_i = 0.139 \, m/\ell$

$[HA] = 0.152 \, m/\ell$

$[H_2O] = \rule{2cm}{0.4pt}$

$R_i = 2.19 \times 10^{-4} \, m/\ell \, SEC$

FIGURE 5L

TABLE XIV

DETERMINATION OF WATER CONTENT DURING INITIAL STAGE OF POLYMERIZATION[a]

Time (sec)	ppm H_2O	% Con.	$[H_2O] \times 10^3$
0	170	0	9.46
20	148	4	8.24
50	137	11	7.62
80	80	138	18	7.68

[a] $[M]_i = 0.6$ m/l; [Acid] $= 0.15$ m/l; Ri 10^3 m/l sec

Conversion and water content do not appear to have significant effects on molecular weight in polymerizations with diethylphosphoric acid in acetonitrile (Fig. 1) and methylene chloride (Table XV), indicating that water is not involved in chain transfer or other reactions in chain propagation and termination. These findings and the difference in the observed effect of water on the polymerization with trifluoroacetic acid (Fig. 1) suggest that retardation of the polymerization by water involves an association of water with the acid catalyst which reduces the concentration of protons available for association with monomer.

The run with diethylchlorophosphate ($[Mon]_i = 0.287$ m/l; [ECP] $= 1/2$ [Acid] $= 0.148$ m/l); $[H_2O] = 0.14973$ m/l, theoretically leaving 1.73×10^{-3} m/l H_2O to retard polymerization; $R_i = 14.59 \times 10^{-4}$ m/l sec.) involved inclusion of an equimolar amount of water for hydrolysis. In this case the exact amount of water retarding polymerization (theoretically 1.156% of water present initially) is somewhat uncertain owing to the extreme dependence on the accuracy of the amount of diethylchlorophosphate injected. Using the equation $R_i = K_o [Monomer]^a [Acid]_i^b [Water]_i^c$ with two sets of exponents, the calculated overall rate constants of the polymerization with diethylchlorophosphate are in reasonable accord with

TABLE XV

EFFECT OF CONVERSION AND WATER CONTENT ON MOLECULAR WEIGHT

Run II

$[M]_1 = 0.394$ m/l
$[A]_1 = 0.152$ m/l
$[H_2O]_1 = 1.78 \times 10^{-3}$ m/l
$R_1 = 8.45 \times 10^{-4}$ m/l sec

% Conv.	18.8	37.0	46.3
$\bar{M}_n$ [a]	6900	6400	7300

Run III

$[M]_1 = 0.419$ m/l
$[A]_1 = 0.152$ m/l
$[H_2O]_1 = 5.56 \times 10^{-3}$ m/l
$R_1 = 2.68 \times 10^{-4}$ m/l sec

% Conv.	2.2	3.9	7.4	11.5	15.8	19.6	23.3	26.2	28.5
$\bar{M}_n$ [b]	7500	7050	6360	5800	6370	7570	6150	6490	5520

[a] Extrapolated to infinite dilution (Mechrolab VPO).

[b] Single determinations (Mechrolab VPO).

those of the polymerization with diethylphosphoric acid if there was a 0.5% excess in the amount of injected diethylchlorophosphate and this compound hydrolyzes to yield two catalytically effective acids. If $a = 2$, $b = 1$ and $c = 1$, $K_o = 6.20 \times 10^{-5}$ for diethylchlorophosphate, and $K_o = 6.92 \times 10^{-5}$ for diethylphosphoric acid as the catalyst. If $a = 3/4$, $b = 1/4$ and $c = -1$, $K_o = 5.13 \times 10^{-6}$ for diethylchlorophosphate, and $K_o = 4.88 \times 10^{-6}$ for diethylphosphoric acid as the catalyst.

Although the kinetic studies are incomplete, the data indicate that the initial rate of polymerization is proportional to $[\text{Monomer}]^a$ $[\text{Acid}]_i$ $[\text{Water}]_i^{-1}$ where $[\text{Acid}]_i$ and $[\text{Water}]_i$ are initial concentrations and $a = 2$ for most runs, varying from 3/4 to 5 at lower and higher monomer concentrations respectively.

Increased dependency on monomer concentration as the latter is increased has been observed in other cationic polymerizations[1], although we are not aware of another case where this occurs to the same extent as in this instance. It may reflect aggregation of monomer at high concentration. Lithium metal or alkyl catalyzed anionic polymerization[9] and the perchloric acid catalyzed cationic polymerization of styrene[10] are also believed to involve catalyst-monomer aggregates.

The observed rate of polymerization of N-vinylcarbazole polymerization of N-vinylcarbazole polymerization in methylene chloride and a 6:1 mixture of methylene chloride and acetonitrile changes sharply and tends to level off soon after the initial fast rate in a manner similar to that observed by Hayes and Pepper[3] for the polymerization of styrene with sulfuric acid. Polymer yield at the leveling-off point was proportional to initial acid concentration. With N-vinylcarbazole, this yield is also dependent on monomer and water concentrations. This effect would have little or no significance in using the polymerization of

N-vinylcarbazole in a detection scheme, since the latter involves initial polymerization characteristics and the solvent would most likely be one that is similar to acetonitrile which does not have this effect on polymerization (Fig. 2).

It is unusual that water is not consumed in the polymerization and that it retards but does not inhibit polymerization. Water often serves as a cocatalyst in cationic polymerization and accelerates the rate and does not retard the polymerization until its concentration reaches a certain small molar ratio with respect to acid catalyst. Brown and Mathieson[4], in a study of the polymerization of styrene with chloroacetic acids in various solvents in the presence of water, found water to accelerate polymerization in every case except one. Water retarded polymerization when nitromethane was used as the solvent. The exponent of the water dependency in this case was not determined.

Cationic catalysts are often consumed in polymerization. For instance, Brown and Mathieson[4] found one chloroacetic ester end group per polymer molecule, indicating that this occurs by a reaction of the terminal carbonium-ion on the chain with chloroacetic anion. That Bronsted-acid catalyst is not consumed in polymerization of N-vinylcarbazole in methylene chloride and acetonitrile is indicated by the effectiveness of trace catalysis (ineffective if catalyst is consumed), residual catalytic properties of a solution remaining after completion of a polymerization and kinetic data. Initiation of the polymerization of N-vinyl-carbazole may be similar to that proposed for other monomers having a heteroatom attached to a vinyl group[1]. For instance, in the case of vinylethers, it is believed that initiation involves proton addition to the double bond which is facilitated by a greater electron-enrichment of the double bond resulting from the mesomeric effect ($Alk-\overset{+}{O} = CH - CH_2^-$) than a loss of electrons caused by the inductive effect ($Alk \leftarrow O \leftarrow CH = CH_2$) (ref. 1, p. 378). On the other hand,

since the polymerization of N-vinylcarbazole is also catalyzed by weak acids such as phenol which is believed to form 1:1 hydrogen-bonded π-complexes with aromatic hydrocarbons[11], it is also conceivable that a reactive electron-deficient vinyl group is formed as a result of a charge transfer interaction between monomer and the acid catalyst. This would help account for the strikingly similar characteristics of the Bronsted- and π-acid[12,13] catalyzed polymerizations of N-vinylcarbazole. Be this as it may, lack of catalyst consumption indicates protons are regenerated in the course of polymerization, probably by dissociation of π-complex if initiation involves the latter, or by proton elimination being the dominant reaction terminating chain growth if initiation involves proton addition to the vinyl group of N-vinylcarbazole. Proton elimination is a common termination reaction in cationic polymerization[1,2]. In some cases involving lack of catalyst consumption, such as the polymerization of styrene with perchloric acid[3], it is also believed to be a dominant termination reaction. The polymerization of N-vinylcarbazole with boron fluoride etherate is also believed to be terminated mainly by proton detachment (ref. 1, p. 542).

CONCLUSIONS AND RECOMMENDATIONS

It has been demonstrated that the polymerization of N-vinylcarbazole is uniquely susceptible to catalysis by parts per billion of Bronsted acids or compounds which hydrolyze to yield Bronsted acids. Special features of this polymerization, such as lack of catalyst consumption, and, possibly, lack of water consumption. appear to be responsible for this unusual and potentially useful characteristic. A number of questions remain, however, regarding the feasibility of using this polymerization as the basis of a device to detect hydrolyzable phosphorus compounds.

One of the concerns is whether various agents which need to be detected cause a rapid polymerization. The catalytic effect depends in part on the hydrolysis of the agent and if this is slow the polymerization would also be slow. Diethylchlorophosphate, which has been used as a simulant in this investigation, does not appear to cause any problems in this respect. However, with slower hydrolyzing agents, as experience with p-nitrophenyldiethylphosphate indicates, there might be an impractical delay in observing the onset of polymerization. The reported screening tests should be repeated under conditions which have since been found to favor polymerization. GA, in particular, should be retested. The catalytic activities of agents containing P-F and other linkages of particular interest also need to be determined.

Findings regarding the polymerization of N-vinylcarbazole in acetonitrile and methylene chloride and practical considerations indicate that a solvent used in a detection device should preferably have the following characteristics.

1. It should have low volatility.

2. It should facilitate cationic polymerization, e.g. a solvent which solvates ions and polar species, but does not contain functional groups with basic properties in a Bronsted sense. Such a solvent would reduce ion-pairing and other associations which can be expected to hinder access of monomer to cations involved in initiation or propagation of polymerization.

3. It should dissolve monomer and precipitate polymer to have the appearance of a turbidity serve as a means of detecting polymerization.

4. It should be readily purified, particularly with regard to retarding and catalytic impurities.

It seems reasonable to expect that a nitrile solvent with a low vapor pressure under detection conditions, which dissolves monomer and

precipitates polymer, would be the best reaction medium for a detection system, although a good example of such a solvent has not as yet been found. Solvents other than methylene chloride, acetonitrile, and isobutyronitrile were not studied extensively, and preliminary findings were unsatisfactory.

A related problem concerns the tendency of N-vinylcarbazole to polymerize on standing in dry and purified solvents. This polymerization is about four times slower than the polymerization induced by addition of 40 parts per billion of acid. Since it is retarded by water, the polymerization on standing of monomer in solvent is also believed to involve a cationic polymerization caused, in this case, by less than 40 parts per billion of acidic impurities in solvent and monomer. At the conclusion of this program it was found that overnight refluxing of acetonitrile and isobutyronitrile with and followed by fractional distillation from bis(2-methylphenyl)carbodiimide[7] yielded solvents from which monomer solutions were prepared that remained stable in the absence of added catalyst and active on addition catalyst for at least 5 days. This purification procedure has since been adopted with satisfactory results for cationic polymerizations of N-vinylcarbazole with other types of catalysts. Further insurance against instability of solutions of monomer can be obtained by an inclusion of acid deactivators such as pinene which has been found to minimize catalytic effects of airborne Bronsted acids and optimizing selectivity in response to the presence of hydrolyzable phosphoric acid derivatives. Although not tested, it is reasonable to believe that terpenes would also minimize catalytic effects of airborne oxidants such as the halogens and nitrogen oxides[12,13]. There would be dozens of unsaturated terpenes available from which to select the most suitable deactivator, or a combination of selected terpenes could be used.

However, if present kinetic findings indicating that the rate of polymerization is more dependent on monomer than on catalyst concentration, are

borne out by further studies, it may also be worthwhile to consider the possibility of avoiding the need for a solvent by using a monomer in which a branched and/or long alkyl group having polar groups such as the -CN group (to provide a polar reaction medium) is substituted on N-vinylcarbazole in a position such that asymmetry and steric bulk would cause such a monomer to be liquid. The employment of such a monomer would eliminate solvent volatility and impurity problems and can be expected to yield an extremely sensitive means of detecting hydrolyzable phosphorus compounds

EXPERIMENTAL

I. POLYMERIZATION

A. Heterogeneous Polymerization

The heterogeneous polymerizations in acetonitrile were conducted in open unbaked test tubes at room temperature, since no effects attributable to oxygen or carbon dioxide and no significant gain in water content in a 15 min. interval were noted in comparing results of tests with baked, unbaked, stoppered and unstoppered test tubes in the absence and presence of air, oxygen and carbon dioxide at various catalyst and water concentrations. Preweighed amounts of monomer were dissolved in acetonitrile, or monomer in the form of a stock solution was diluted with acetonitrile. Moisture content was adjusted when necessary by adding water in the form of a stock solution in acetonitrile. Catalyst was usually injected with a hypodermic syringe in undiluted form or from a stock solution in acetonitrile. Total volume of acetonitrile used in a polymerization was maintained at 5 ml. Polymerization time was measured from the time catalyst was injected. In some of the earlier cases the polymerizations were shortstopped and polymers worked up by precipitation with acetone, but in most cases methanol was used for these purposes. Polymer was collected on a

preweighed sintered glass filter funnel, and weighed for yield determination after vacuum drying overnight at room temperature.

B. Homogeneous Polymerization

Some of the homogeneous polymerizations in methylene chloride and mixtures of this solvent with acetonitrile were conducted in a similar manner, but in most cases they were performed under nitrogen in a 250 ml. 3-neck flask charged with 7 to 14 g monomer, 150 ml. solvent and 1 to 3 ml. catalyst, and equipped with a mechanical stirrer, nitrogen in- and outlets, a serum cap through which to introduce catalyst, and a stopcock at the bottom of the flask for periodic sample withdrawal. Samples were withdrawn at 15 sec (for the first 2 to 3 minutes), 30 sec and 1 min intervals after injection of catalyst. At no time was monomer solution allowed to stand for more than 10 mins before injection of catalyst. About 21 to 23 5 ml. samples were withdrawn per run. Polymer yields were determined gravimetrically. The amounts of periodically withdrawn samples of the polymerization mixture were determined by collecting the samples in preweighed vials containing about 1 ml. methanol, which was sufficient to shortstop the polymerization but not to precipitate the polymer, and reweighing the mixtures in the vials. The polymer was then worked up reproducibly by rapidly adding solutions of the samples in methylene chloride and methanol to beakers containing 100 ml magnetically agitated methanol, collecting precipitated polymer samples on preweighed sintered glass filter funnels, and weighing them for yield determinations after drying overnight in a vacuum oven at room temperature. Water content of monomer and solvent were combined to determine total water content and in some cases the water content of monomer solution was determined before and after polymerization.

II. CATALYSTS

Diethylchlorophosphate and dibutylchlorophosphate, obtained from Victor Chemicals, were vacuum distilled. Fractions distilling at 57°C/2.2 mm Hg and 86°C/0.9 mm Hg respectively were collected. Other catalysts were used as received. The neutralization equivalent of diethylphosphoric acid obtained from Victor Chemicals was 154.0 (determined with a pH meter) which compares favorably with a theoretical value of 154.1.

III. MONOMER

N-vinylcarbazole obtained from Matheson Co. was recrystallized in 50 g lots from a carbon-black-treated solution containing 10% water, or dissolved and treated with carbon black in ethanol, and recovered in ca. 60% yield by concentration under vacuum with a rotary flash evaporator, to yield a product melting at 64.0°C after being ground and vacuum dried overnight at room temperature. The water content of the product at this stage varied from ca. 100 to 900 ppm. For experiments requiring a lower water content, the monomer was further freeze-dried at -20°C (to minimize a tendency to polymerize in the solid state) for a week on a vacuum line with liquid nitrogen traps at 10^{-4} mm Hg. Attempts to determine the resulting water content were unsuccessful, possibly because the large sample of oxidizable monomer required to determine a low water content interferes with the redox reactions involved in the Karl Fisher titration.

IV. SOLVENTS

Spectroquality acetonitrile obtained from Matheson Co. was distilled from phosphorus pentoxide to reduce the water content from ca. 600 ppm to < 5 ppm, followed by a slow passage through a 100 x 25 mm column of finely powdered calcium hydride to remove an acidic impurity which was

occasionally produced, possibly, owing to the volatility of phosphorus pentoxide (ref. 1, p. 683). It caused no polymerization of dried monomer for at least 60 mins. This is a time consuming procedure. Distillation of acetonitrile and isobutyronitrile from calcium hydride, however, yielded solvents in which monomer was deactivated on standing for unknown reasons. At the conclusion of this program, when it was too late for general adoption, isobutyronitrile (Eastman) and acetonitrile of more satisfactory polymerization quality were obtained by an overnight reflux with and then a distillation from vacuum distilled bis(2-methylphenyl)carbodiimide.

Reagent grade methylene chloride obtained from Fisher Scientific Co. was distilled from phosphorus pentoxide to reduce the water content from 270 ppm to < 5 ppm. It yielded no precipitate when treated with aqueous silver nitrate and it did not cause polymerization of dried monomer for two hours. Methylene chloride of similar quality was obtained by reflux and distillation from calcium hydride.
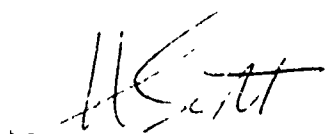
Purified solvents were stored under nitrogen pressure in beverage bottles baked for several days at 150°C, cooled under nitrogen, and capped with crown caps having a hole in the center and an extracted self-sealing rubber liner for withdrawal of solvent with a hypodermic syringe. No increase in water content was noted after a month's storage.

V. ANALYSES

Water content was determined by the Karl Fisher titration using a Beckman KF-3 Aquameter and a blanket of Airco prepurified nitrogen dried by passage through 4' x 2-1/2" column of Linde 3A molecular sieves. At the end of the program it was found that a more economical and very much simpler Labindustries Aquameter yielded comparable results without requiring time consuming mechanical adjustment during standardization procedures required

every day Karl Fisher reagent is used.

Elemental analyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

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ACCESSION NO.

1. Organophosphorus Compounds - Bronsted acids - N-Vinylcarbazole - Polymerization

2. Contract DA-18-108-AMC-169(A)

AD

The Franklin Institute Research Laboratories, Philadelphia, Pa. 19103

A NEW TYPE OF POLYMERIZATION INVOLVING ORGANOPHOSPHORUS COMPOUNDS - H. Scott, T. P. Konen and M. M. Labes

Final Report, 24 February 1965, pp 51 - 15 tables
Contract DA-18-108-AMC-169(A)

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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Franklin Institute Research Laboratories	UNCLASSIFIED
	2b GROUP ---

3 REPORT TITLE

A NEW TYPE OF POLYMERIZATION INVOLVING ORGANOPHOSPHORUS
COMPOUNDS AS CATALYSTS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Report   1 June 1963 to 27 January 1965

5 AUTHOR(S) *(Last name, first name, initial)*

Scott, H., Konen, T. P. and Labes, M. M.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
24 February 1965	51	13

8a CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DA-18-108 AMC-169	
b. PROJECT NO F-B2111	F-B2111
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) ---
d.	

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

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DD FORM 1473 1 JAN 64